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**WO 02/49678 A2**

(54) Title: METHOD AND APPARATUS FOR MANUFACTURING POLYMER FIBER SHELLS VIA ELECTROSPINNING

(57) Abstract: An apparatus for manufacturing a polymer fiber shell from liquefied polymer is provided. The apparatus includes: (a) a precipitation electrode being for generating the polymer fiber shell thereupon; (b) a dispenser, being at a first potential relative to the precipitation electrode so as to generate an electric field between the precipitation electrode and the dispenser, the dispenser being for: (i) charging the liquefied polymer thereby providing a charged liquefied polymer; and (ii) dispensing the charged liquefied polymer in a direction of the precipitation electrode; and (c) a subsidiary electrode being at a second potential relative to the precipitation electrode, the subsidiary electrode being for modifying the electric field between the precipitation electrode and the dispenser.

## METHOD AND APPARATUS FOR MANUFACTURING POLYMER FIBER SHELLS VIA ELECTROSPINNING

### FIELD AND BACKGROUND OF THE INVENTION

5       The present invention relates to a method and apparatus for manufacturing polymer fiber shells via electrospinning.

Polymer fiber shells such as tubular shaped products, are used in the medical industry for various utilities including esophageal grafts, vascular grafts, stent coats and like.

10     Numerous methods for manufacturing polymer fiber shells suitable for medical applications are known in the art, including, for example, various injection molding methods, mandrel assisted extrusion or formation and various weaving techniques.

Production of polymer fiber shells suitable for use as vascular grafts 15 . is particularly difficult, since such grafts must withstand high and pulsatile blood pressures while, at the same time, be elastic and biocompatible.

Vascular grafts known in the art typically have a microporous structure that in general allows tissue growth and cell endothelization, thus contributing to long term engraftment and patency of the graft.

20     In vascular grafts, tissue ingrowth and cell endothelization is typically enhanced with increased porosity. However, increasing the porosity of vascular grafts leads to a considerable reduction of the mechanical and tensile strength of the graft, and as a consequence to a reduction in the functionality thereof.

25     Electrospinning has been used for generating various products for medical applications, *e.g.*, wound dressings, prosthetic devices, and vascular grafts as well as for industrial use, *e.g.*, electrolytic cell diaphragms, battery separators, and fuel cell components. It has already been proposed to produce by electrospinning products having the 30 appearance of shells. For example, U.S. Patent No. 4,323,525 discloses a

method of preparing a tubular product by electrostatically spinning a fiber forming material and collecting the resulting spun fibers on a rotating mandrel. U.S. Patent No. 4,552,707 discloses a varying rotation rate mandrel which controls the "anisotropy extent" of fiber orientation of the final product. Additional examples of tubular shaped products and a like are disclosed, e.g., in U.S. Patent Nos. 4,043,331, 4,127,706, 4,143,196, 4,223,101, 4,230,650 and 4,345,414.

The process of electrospinning creates a fine stream or jet of liquid that upon proper evaporation yields a non-woven fiber structure. The fine stream of liquid is produced by pulling a small amount of a liquefied polymer (either polymer dissolved in solvent (polymer solution) or melted polymer) through space using electrical forces. The produced fibers are then collected on a suitably located precipitation device, such as a mandrel to form tubular structures. In the case of a melted polymer which is normally solid at room temperature, the hardening procedure may be mere cooling, however other procedures such as chemical hardening or evaporation of solvent may also be employed.

In electrospinning, an electric field with high filed lines density (*i.e.*, having large magnitude per unit volume) may results in a corona discharge near the precipitation device, and consequently prevent fibers from being collected by the precipitation device. The filed lines density of an electric field is determined *inter alia* by the geometry of the precipitation device; in particular, sharp edges on the precipitation device increase the effect of corona discharge.

In addition, due to the effect of electric dipole rotation along the electric field maximal strength vector in the vicinity of the mandrel, products with at least a section with a small radius of curvature are coated coaxially by the fibers. Such structural fiber formation considerably reduces the radial tensile strength of a spun product, which, in the case of

vascular grafts, is necessary for withstanding pressures generated by blood flow.

Various electrospinning based manufacturing methods for generating vascular grafts are known in the prior art, see, for example, U.S. Patent Nos. 5 4,044,404, 4,323,525, 4,738,740, 4,743,252, and 5,575,818. However, such methods suffer from the above inherent limitations which limit the use thereof when generating intricate profile fiber shells.

Hence, although electrospinning can be efficiently used for generating large diameter shells, the nature of the electrospinning process 10 prevents efficient generation of products having an intricate profile and/or small diameter, such as vascular grafts. In particular, since porosity and radial strength are conflicting, prior art electrospinning methods cannot be effectively used for manufacturing vascular grafts having both characteristics.

15 There is thus a widely recognized need for, and it would be highly advantageous to have, a method and apparatus for manufacturing polymer fiber shells via electrospinning devoid of the above limitations.

#### SUMMARY OF THE INVENTION

20 According to one aspect of the present invention there is provided an apparatus for manufacturing polymer fiber shells from liquefied polymer, the apparatus comprising: (a) a precipitation electrode being for generating the polymer fiber shell thereupon; (b) a dispenser, being at a first potential relative to the precipitation electrode so as to generate an electric field 25 between the precipitation electrode and the dispenser, the dispenser being for: (i) charging the liquefied polymer thereby providing a charged liquefied polymer; and (ii) dispensing the charged liquefied polymer in a direction of the precipitation electrode; and (c) a subsidiary electrode being at a second potential relative to the precipitation electrode, the subsidiary

electrode being for modifying the electric field between the precipitation electrode and the dispenser.

According to another aspect of the present invention there is provided a method for forming a liquefied polymer into a non-woven polymer fiber shells, the method comprising: (a) charging the liquefied polymer thereby producing a charged liquefied polymer; (b) subjecting the charged liquefied polymer to a first electric field; (c) dispensing the charged liquefied polymer within the first electric field in a direction of a precipitation electrode, the precipitation electrode being designed and configured for generating the polymer fiber shell; (d) providing a second electric field being for modifying the first electric field; and (e) using the precipitation electrode to collect the charged liquefied polymer thereupon, thereby forming the non-woven polymer fiber shell.

According to further features in preferred embodiments of the invention described below, the first electric field is defined between the precipitation electrode and a dispensing electrode being at a first potential relative to the precipitation electrode.

According to still further features in the described preferred embodiments step (c) is effected by dispensing the charged liquefied polymer from the dispensing electrode.

According to still further features in the described preferred embodiments the second electric field is defined by a subsidiary electrode being at a second potential relative to the precipitation electrode.

According to still further features in the described preferred embodiments the subsidiary electrode serves for reducing non-uniformities in the first electric field

According to still further features in the described preferred embodiments the subsidiary electrode serves for controlling fiber orientation of the polymer fiber shell generated upon the precipitation electrode.

According to still further features in the described preferred embodiments the subsidiary electrode serves to minimize a volume charge generated between the dispenser and the precipitation electrode.

According to still further features in the described preferred 5 embodiments the method further comprising moving the subsidiary electrode along the precipitation electrode during step (e).

According to still further features in the described preferred embodiments the method further comprising moving the dispensing electrode along the precipitation electrode during step (c).

10 According to still further features in the described preferred embodiments the method further comprising synchronizing the motion of the dispensing electrode and the subsidiary electrode along the precipitation electrode.

15 According to still further features in the described preferred embodiments the dispenser comprises a mechanism for forming a jet of the charged liquefied polymer.

According to still further features in the described preferred embodiments the apparatus further comprising a bath for holding the liquefied polymer.

20 According to still further features in the described preferred embodiments the mechanism for forming a jet of the charged liquefied polymer includes a dispensing electrode.

25 According to still further features in the described preferred embodiments the dispenser is operative to move along a length of the precipitation electrode.

According to still further features in the described preferred embodiments the precipitation electrode includes at least one rotating mandrel.

30 According to still further features in the described preferred embodiments the rotating mandrel is a cylindrical mandrel.

According to still further features in the described preferred embodiments the rotating mandrel is an intricate-profile mandrel.

According to still further features in the described preferred embodiments the intricate-profile mandrel includes sharp structural elements.

According to still further features in the described preferred embodiments the cylindrical mandrel is of a diameter selected from a range of 0.1 to 20 millimeters.

According to still further features in the described preferred embodiments the precipitation electrode includes at least one structural element selected from the group consisting of a protrusion, an orifice, a groove, and a grind.

According to still further features in the described preferred embodiments the subsidiary electrode is of a shape selected from the group consisting of a plane, a cylinder, a torus and a wire.

According to still further features in the described preferred embodiments the subsidiary electrode is operative to move along a length of the precipitation electrode.

According to still further features in the described preferred embodiments the subsidiary electrode is tilted at angle with respect to a longitudinal axis of the precipitation electrode, the angle is ranging between 45 and 90 degrees.

According to still further features in the described preferred embodiments the subsidiary electrode is positioned at a distance of 5 - 70 millimeters from the precipitation electrode.

According to still further features in the described preferred embodiments the subsidiary electrode is positioned at a distance  $\delta$  from the precipitation electrode,  $\delta$  being equal to  $12\beta R(1-V_2/V_1)$ , where  $\beta$  is a constant ranging between about 0.7 and about 0.9,  $R$  is the curvature-radius

of the polymer fiber shell formed on the precipitation electrode,  $V_1$  is the first potential and  $V_2$  is the second potential.

According to yet another aspect of the present invention there is provided an apparatus for manufacturing a polymer fiber shells from liquefied polymer, the apparatus comprising: (a) a dispenser, for: (i) charging the liquefied polymer thereby providing a charged liquefied polymer; and (ii) dispensing the charged liquefied polymer; and (b) a precipitation electrode being at a potential relative to the dispenser thereby generating an electric field between the precipitation electrode and the dispenser, the precipitation electrode being for collecting the charged liquefied polymer drawn by the electric field, to thereby form the polymer fiber shell thereupon, wherein the precipitation electrode is designed so as to reduce non-uniformities in the electric field.

According to still further features in the described preferred embodiments the precipitation electrode is formed from a combination of electroconductive and non-electroconductive materials.

According to still further features in the described preferred embodiments a surface of the precipitation electrode is formed by a predetermined pattern of the electroconductive and non-electroconductive materials.

According to still further features in the described preferred embodiments the precipitation electrode is formed from at least two layers.

According to still further features in the described preferred embodiments the at least two layers include an electroconductive layer and a partial electroconductive layer.

According to still further features in the described preferred embodiments the partial electroconductive layer is partial electroconductive layer is formed from a combination of an electroconductive material and at least one dielectric material.

According to still further features in the described preferred embodiments the dielectric material is selected from a group consisting of polyamide and polyacrylonitrile and polytetrafluoroethylene.

According to still further features in the described preferred 5 embodiments the dielectric material is Titanium Nitride.

According to still further features in the described preferred embodiments the partial electroconductive layer, is selected of a thickness ranging between 0.1 to 90 microns.

The present invention successfully addresses the shortcomings of the 10 presently known configurations by providing an electrospinning apparatus and method capable of fabricating a non-woven polymer fiber shell which can be used in vascular grafts.

#### BRIEF DESCRIPTION OF THE DRAWINGS

15 The invention is herein described, by way of example only, with reference to the accompanying drawings. With specific reference now to the drawings in detail, it is stressed that the particulars shown are by way of example and for purposes of illustrative discussion of the preferred embodiments of the present invention only, and are presented in the cause 20 of providing what is believed to be the most useful and readily understood description of the principles and conceptual aspects of the invention. In this regard, no attempt is made to show structural details of the invention in more detail than is necessary for a fundamental understanding of the invention, the description taken with the drawings making apparent to those skilled in the art how the several forms of the invention may be embodied 25 in practice.

In the drawings:

FIG. 1 is a schematic illustration of a prior art electrospinning apparatus;

FIG. 2 is a schematic illustration of an electrospinning apparatus which includes a subsidiary electrode according to the teachings of the present invention;

FIG. 3 is a schematic illustration of an electrospinning apparatus 5 which includes a planar subsidiary electrode according to the teachings of the present invention;

FIG. 4 is a schematic illustration of an electrospinning apparatus which includes a cylindrical subsidiary electrode according to the teachings of the present invention;

10 FIG. 5 is a schematic illustration of an electrospinning apparatus which includes a linear subsidiary electrode according to the teachings of the present invention;

15 FIG. 6 is a schematic illustration of an electrospinning apparatus which includes a composite subsidiary electrode according to the teachings of the present invention;

FIG. 7 is an electron microscope image of material spun using conventional electrospinning techniques;

20 FIG. 8 is an electron microscope image of material spun using an apparatus which incorporates a flat subsidiary electrode, positioned 20 millimeters from the mandrel, according to the teachings of the present invention;

25 FIG. 9 is an electron microscope image of material spun using an apparatus which incorporates a flat subsidiary electrode, positioned 9 millimeters from the mandrel, according to the teachings of the present invention; and

FIG. 10 is an electron microscope image of polar-oriented material spun using an apparatus which incorporates a linear subsidiary electrode according to the teachings of the present invention.

DESCRIPTION OF THE PREFERRED EMBODIMENTS

The present invention is of a method and an apparatus for manufacturing a polymer fiber shell using electrospinning. Specifically, the present invention can be used to manufacture intricate-profile products and 5 vascular grafts of small to large diameter via electrospinning.

For purposes of better understanding the present invention, as illustrated in Figures 2-10 of the drawings, reference is first made to the construction and operation of a conventional (*i.e.*, prior art) electrospinning apparatus as illustrated in Figure 1.

10 Figure 1 illustrates an apparatus for manufacturing a tubular structure using a conventional electrospinning apparatus, which is referred to herein as apparatus 10.

15 Apparatus 10 includes a dispenser 12 which can be, for example, a bath provided with capillary apertures 14. Dispenser 12 serves for storing the polymer to be spun in a liquid form. Dispenser 12 is positioned at a predetermined distance from a precipitation electrode 16.

20 Precipitation electrode 16 serves for generating the tubular structure thereupon. Precipitation electrode 16 is typically manufactured in the form of a mandrel or any other cylindrical structure. Precipitation electrode 16 is rotated by a mechanism such that a tubular structure is formed when coated with the polymer.

25 Dispenser 12 is typically grounded, while precipitation electrode 16 is connected to a source of high voltage preferably of negative polarity, thus forming an electric field between dispenser 12 and precipitation electrode 16. Alternatively, precipitation electrode 16 can be grounded while dispenser 12 is connected to a source of high voltage, preferably with positive polarity.

30 To generate a tubular structure, a liquefied polymer (e.g., melted polymer or dissolved polymer) is extruded, for example under the action of hydrostatic pressure, through capillary apertures 14 of dispenser 12. As

soon as meniscus forms from the extruded liquefied polymer, a process of solvent evaporation or cooling starts which is accompanied by the creation of capsules with a semi-rigid envelope or crust. An electric field, occasionally accompanied by unipolar corona discharge in the area of dispenser 12, is generated by the potential difference between dispenser 12 and precipitation electrode 16. Because the liquefied polymer possesses a certain degree of electrical conductivity, the above-described capsules become charged. Electric forces of repulsion within the capsules lead to a drastic increase in hydrostatic pressure. The semi-rigid envelopes are stretched, and a number of point micro-ruptures are formed on the surface of each envelope leading to spraying of ultra-thin jets of liquefied polymer from dispenser 12.

The charges tend to distribute along the jets, thus preventing existence of any non-zero component of electric field inside the jet. Thus, a conduction current flows along the jets, which results in the accumulation of (different sign) free charges on the liquefied polymer surface.

Under the effect of a Coulomb force, the jets depart from the dispenser 12 and travel towards the opposite polarity electrode, *i.e.*, precipitation electrode 16. Moving with high velocity in the inter-electrode space, the jet cools or solvent therein evaporates, thus forming fibers which are collected on the surface of precipitation electrode 16. Since electrode 16 is rotating the charged fibers form a tubular shape.

When using mandrels being at least partially with small radius of curvature, the orientation of the electric field maximal strength vector is such that precipitation electrode 16 is coated coaxially by the fibers. Thus, small diameter products, have limited radial strength when manufactured via existing electrospinning methods, as described above.

When using mandrels with sharp edges and/or variously shaped and sized recesses, the electric field magnitude in the vicinity of precipitation electrode 16 may exceed the air electric strength (about 30 kV/cm), and a

corona discharge may develop in the area of precipitation electrode 16. The effect of corona discharge decreases the coating efficiency of the process as described hereinbelow, and may even result in a total inability of fibers to be collected upon precipitation electrode 16.

5       Corona discharge initiation is accompanied by the generation of a considerable amount of air ions having opposite charge sign with respect to the charged fibers. Since an electric force is directed with respect to the polarity of charges on which it acts, these ions start to move at the opposite direction to fibers motion *i.e.*, from precipitation electrode 16 towards 10 dispenser 12. Consequently, a portion of these ions generate a volume charge (ion cloud), non-uniformly distributed in the inter-electrode space, thereby causing electric field lines to partially close on the volume charge rather than on precipitation electrode 16. Moreover, the existence of an 15 opposite volume charge in the inter-electrode space, decreases the electric force on the fibers, thus resulting in a large amount of fibers accumulating in the inter-electrode space and gradually settling under gravity force. It will be appreciated that such an effect leads to a low-efficiency process of fiber coating.

Using an infinite-length/radius cylinder as a precipitation electrode 20 16 diminishes the effect described above. However, this effect is severe and limiting when small radii or complicated mandrels are employed for fabricating small radius or intricate-profile structures.

Before explaining at least one embodiment of the invention in detail, it is to be understood that the invention is not limited in its application to 25 the details of construction and the arrangement of the components set forth in the following description or illustrated in the drawings. The invention is capable of other embodiments or of being practiced or carried out in various ways. Also, it is to be understood that the phraseology and terminology employed herein is for the purpose of description and should not be 30 regarded as limiting.

While reducing the present invention to practice, it was uncovered that the use of a third electrode within an electrospinning apparatus enables to control the electric field generated between the dispenser and precipitation electrode. Specifically, a third electrode may either 5 substantially decreases non-uniformities in the electric field or provides for controlled fiber orientation upon deposition.

Thus, according to the present invention there is provided an apparatus for manufacturing a polymer fiber shell from a liquefied polymer, which apparatus is referred to herein as apparatus 20.

As shown in Figure 2, apparatus 20 includes a precipitation electrode 22 which serves for generating the polymer fiber shell thereupon. Precipitation electrode 22 can be, for example, a mandrel of uniform or varying radius, which may include some structural elements such as, but not limited to, protrusions, orifices and grooves. The surface of precipitation 15 electrode 22 may also contain grinds. The diameter of the mandrel may vary from about 0.1 millimeter up to about 20 millimeters depending on the diameter of the polymer fiber shell to be spun thereupon.

Apparatus 20 further includes a dispenser 24, which is at a first potential relative to precipitation electrode 22. Such a potential can be 20 generated by grounding dispenser 24, and connecting a source of high voltage with negative polarity to precipitation electrode 22.

Alternatively, precipitation electrode 22 can be grounded while dispenser 24 is connected to a source of high voltage with positive polarity. In any case, an absolute value for the potential difference between dispenser 25 24 and precipitation electrode 22 may range between about 10 kV and about 100 kV.

The potential difference between dispenser 24 and precipitation electrode 22 ensures that an electric field is maintained therebetween, which electric field is important for the electrospinning process as described 30 hereinabove.

Dispenser 24 serves for charging the liquefied polymer, thereby providing a charged liquefied polymer and dispensing the charged liquefied polymer in a direction of precipitation electrode 22. Dispenser 24 may also include a mechanism for moving it along a longitudinal axis of precipitation electrode 22, thus enabling dispensing of the charged liquefied polymer at various points along the longitudinal axis of precipitation electrode 22.

The charged liquefied polymer may be, for example polyurethane, polyester, polyolefin, polymethyl methacrylate, polyvinyl aromatic, polyvinyl ester, polyamide, polyimide, polyether, polycarbonate, polyacrylonitrile, polyvinyl pyrrolidone, polyethylene oxide, poly (L-lactic acid), poly (lactide-CD-glycoside), polycaprolactone, polyphosphate ester, poly (glycolic acid), poly (DL-lactic acid), and some copolymers. Biomolecules such as DNA, silk, chitozan and cellulose may also be used. Improved charging of the polymer may also be required. Improved charging is effected according to the present invention by mixing the liquefied polymer with a charge control agent (e.g., a dipolar additive) to form, for example, a polymer-dipolar additive complex which apparently better interacts with ionized air molecules formed under the influence of the electric field. It is assumed, in a non-limiting fashion, that the extra-charge attributed to the newly formed fibers is responsible for their more homogenous precipitation on the precipitation electrode, wherein a fiber is better attracted to a local maximum, which is a local position most under represented by older precipitated fibers, which keep their charge for 5-10 minutes. The charge control agent is typically added in the grams equivalent per liter range, say, in the range of from about 0.001 N to about 0.1 N, depending on the respective molecular weights of the polymer and the charge control agent used.

U.S. Pat. Nos. 5,726,107; 5,554,722; and 5,558,809 teach the use of charge control agents in combination with polycondensation processes in the production of electret fibers, which are fibers characterized in a

permanent electric charge, using melt spinning and other processes devoid of the use of an precipitation electrode. A charge control agent is added in such a way that it is incorporated into the melted or partially melted fibers and remains incorporated therein to provide the fibers with electrostatic 5 charge which is not dissipating for prolonged time periods, say months.

In a preferred embodiment of the present invention, the charge control agent transiently binds to the outer surface of the fibers and therefore the charge dissipates shortly thereafter (within minutes). This is because polycondensation is not exercised at all such the chemical 10 interaction between the agent and the polymer is absent, and further due to the low concentration of charge control agent employed. The resulting shell is therefore substantially charge free.

Suitable charge control agents include, but are not limited to, mono- and poly-cyclic radicals that can bind to the polymer molecule via, for 15 example, -C=C-, =C-SH- or -CO-NH- groups, including biscationic amides, phenol and uryl sulfide derivatives, metal complex compounds, triphenylmethanes, dimethylimidazole and ethoxytrimethylsians.

Typically, the charged liquefied polymer is dispensed as a liquid jet, moving at high velocity under electrical forces caused by the electric field. 20 Thus, dispenser 24 typically includes a bath for holding the liquefied polymer and a mechanism for forming a jet, which mechanism may be, for example, a dispensing electrode.

Apparatus 20 further includes at least one subsidiary electrode 26 which is at a second potential relative to precipitation electrode 22. 25 Subsidiary electrode 26 serves for controlling the direction and magnitude of the electric field between precipitation electrode 22 and dispenser 24 and as such, subsidiary electrode 26 can be used to control the orientation of polymer fibers deposited on precipitation electrode 22. In some embodiments, subsidiary electrode 26 serves as a supplementary screening 30 electrode. Broadly stated, use of screening results in decreasing the coating

precipitation factor, which is particularly important upon mandrels having at least a section of small radii of curvature.

The size, shape, position and number of subsidiary electrode 26 is selected so as to maximize the coating precipitation factor, while 5 minimizing the effect of corona discharge in the area of precipitation electrode 22 and/or so as to provide for controlled fiber orientation upon deposition.

According to one preferred embodiment of the present invention, subsidiary electrode 26 is positioned 5-70 mm away from precipitation 10 electrode 22.

Preferably, such a distance is selected according to the following:

$$\delta = 12\beta R(1 - V_2/V_1) \quad (\text{Eq. 1})$$

15 where  $\beta$  is a dimensionless constant named a fiber-charge accounting factor, which ranges between about 0.7 and about 0.9,  $R$  is the curvature-radius of precipitation electrode 22,  $V_1$  is the potential difference between dispenser 24 and precipitation electrode 22 and  $V_2$  is the potential difference between subsidiary electrode 26 and precipitation electrode 22.

20 Subsidiary electrode 26 may include a mechanism for moving it along a longitudinal axis of precipitation electrode 22. Such a mechanism may be in use when enhanced control over fiber orientation is required.

25 It will be appreciated that in an apparatus in which both dispenser 24 and subsidiary electrode 26 are capable of such longitudinal motion, such motion may be either independent or synchronized.

Subsidiary electrode 26 may also be tilted through an angle of 45-90 degrees with respect to the longitudinal axis of precipitation electrode 22. Such tilting may be used to provide for controlled fiber orientation upon deposition, hence to control the radial strength of the manufactured shell; 30 specifically, large angles result in higher radial strength.

In addition to positioning, the shape and size of electrode 26 may also determine the quality of the shell formed by apparatus 20. Thus, electrode 26 may be fabricated in a variety of shapes each serving a specific purpose. Electrode shapes which can be used with apparatus 20 of the 5 present invention include, but are not limited to, a plane, a cylinder, a torus a rod, a knife, an arc or a ring.

An apparatus 20 which includes a subsidiary electrode 26 of a cylindrical (Figure 4) or a flat shape (Figure 3) enables manufacturing intricate-profile products being at least partially with small radius of 10 curvature, which radius may range between 0.025 millimeters and 5 millimeters. As can be seen in Figures 8-9 (further described in the Examples section), the coating of such structures is characterized by random-oriented (Figure 8) or even polar-oriented (Figure 9) fibers, as opposed to an axial coating which is typical for small curvature products 15 manufactured via existing electrospinning methods as demonstrated in Figure 7 (further described in the Examples section).

Preferably, when a surface of large curvature is used as subsidiary electrode 26, as is the case above, the distance between subsidiary electrode 26 and precipitation electrode 22 can be determined as  $\delta/x$  where  $x$  is a 20 factor ranging between 1.8 and 2, and where  $\delta$  is as defined by Equation 1 above.

Thus, positioning and/or shape of electrode 26 determines fiber orientation in the polymer fiber shell formed.

The ability to control fiber orientation is important when fabricating 25 vascular grafts in which a high radial strength and elasticity is important. It will be appreciated that a polar oriented structure can generally be obtained also by wet spinning methods, however in wet spinning methods the fibers are thicker than those used by electrospinning by at least an order of magnitude.

Control over fiber orientation is also advantageous when fabricating composite polymer fiber shells which are manufactured by sequential deposition of several different fiber materials.

Reference is now made to Figure 5, which illustrates an apparatus 20  
5 which utilizes a linear (e.g., a rod, a knife, an arc or a ring) subsidiary electrode 26.

The effect of subsidiary electrode 26 of linear shape is based on the distortion it introduces to the electric field in an area adjacent to precipitation electrode 22. For maximum effect the diameter of subsidiary 10 electrode 26 must be considerably smaller than that of precipitation electrode 22, yet large enough to avoid generation of a significant corona discharge. Fiber coating generated by apparatus 20 utilizing a linear subsidiary electrode 26 is illustrated by Figure 10 which is further described in the Examples section hereinunder.

15 Thus, the present invention provides an electrospinning apparatus in which the electric field is under substantial control, thereby providing either random or predetermined fibers orientation.

Although the use of at least one subsidiary electrode is presently preferred, field non-uniformities can also be at least partially overcome by 20 providing a composite precipitation electrode.

As illustrated in Figure 6, precipitation electrode 34 of apparatus 30 having a dispenser 32 can be designed and configured so as to reduce non-uniformities in the electric field.

To overcome field non-uniformities, precipitation electrode 34 is 25 fabricated from at least two layers of materials, an inner layer 36 made of electroconductive material and an outer layer 38 made of a material having high dielectric properties. Such a fabrication design results in a considerable increase of corona discharge threshold thus considerably reducing corona discharge from precipitation electrode 34.

- Materials suitable for use with outer layer 38 of precipitation electrode 34, can be ceramic materials *e.g.*, Titanium Nitride, Aluminum Oxide and the like, or polymer materials *e.g.*, polyamide, polyacrylonitrile, polytetrafluoroethylene and the like. The thickness of outer layer 38 depends on the dielectric properties of the material from which it is made and can vary from less than one micron, in the case of, for example, a Titanium Nitride layer, or tens of microns, in the case of, for example, polytetrafluoroethylene, polyamide or polyacrylonitrile layer. In addition to diminishing corona discharge this precipitation electrode configuration enables easier separation of formed structures therefrom. Thus, according to this configuration outer layer 38 of precipitation electrode 34 can also be configured for facilitating the removal of the final product from the mandrel.
- Additional objects, advantages, and novel features of the present invention will become apparent to one ordinarily skilled in the art upon examination of the following examples, which are not intended to be limiting. Additionally, each of the various embodiments and aspects of the present invention as delineated hereinabove and as claimed in the claims section below finds experimental support in the following examples.

## EXAMPLES

Reference is now made to the following examples, which together with the above descriptions, illustrate the invention in a non limiting fashion.

### *Electrospinning Material*

A polycarbonate resin grade Caliper 2071 was purchased from Daw Chemical Co. This Polymer is characterized as having good fiber forming

20

abilities and is convenient for electrospinning. Chloroform was used as solvent in all of the examples described hereinbelow.

### ***EXAMPLE 1***

#### **5       *Axial Covering Using Conventional Electrospinning Method***

Reference is now made to Figure 7, which is an example of non-randomized covering of thin mandrels via conventional electrospinning. A 3-mm cylindrical mandrel was covered by polycarbonate fiber using prior art electrospinning approaches. Figure 7 is 10 an electron microscope image of the final product, in which axial fiber orientation is well evident. Due to non-uniformities in the electric field, the fibers, while still in motion in the inter-electrode space, are oriented in conformity with the field configuration, and the obtained tubular structure exhibits axial orientation of fibers, and as such is characterized by axial, as 15 opposed to radial strength.

### ***EXAMPLE 2***

#### ***Random Covering Using Flat Subsidiary Electrode***

An apparatus constructed and operative in accordance with the 20 teachings of the present invention incorporating a flat subsidiary electrode positioned 20 millimeters from the mandrel and having the same potential as the mandrel was used to spin a polycarbonate tubular structure of a 3 mm radius. As is evident from Figure 8, the presence of a subsidiary electrode randomizes fibers orientation.

25

### ***EXAMPLE 3***

#### ***Polar-Oriented Covering Using Flat Subsidiary electrode***

An apparatus constructed and operative in accordance with the 30 teachings of the present invention incorporating a flat subsidiary electrode positioned 9 millimeters from the mandrel and being at a potential

difference of 5 kV from the mandrel was used to spin a polycarbonate tubular structure of a 3 mm radius.

As illustrated by Figure 9, reduction of equalizing electrode-mandrel distance results in polar-oriented covering. Thus, by keeping subsidiary 5 electrode and mandrel within a relatively small distance, while providing a non-zero potential difference therebetween, leads to slow or no fiber charge dissipation and, as a result, the inter-electrode space becomes populated with fiber which are held statically in a stretched position, oriented perpendicular to mandrel symmetry axis. Once stretched, the fibers are 10 gradually coiled around the rotating mandrel, generating a polar-oriented structure.

#### EXAMPLE 4

##### *Predefined Oriented Covering Using Linear Subsidiary electrode*

Figure 10 illustrates result obtained from an apparatus configuration 15 which may be employed in order to obtain a predefined oriented structural fiber covering.

An apparatus which includes an elliptical subsidiary electrode and a dispenser both moving along the longitudinal axis of the mandrel in a reciprocating synchronous movement was used to coat a 3-mm cylindrical 20 mandrel with polycarbonate fiber. The subsidiary electrode had a large diameter of 120 mm, a small diameter of 117.6 mm and a thickness of 1.2 mm. The subsidiary electrode was positioned 15 mm from the mandrel, at an 80 ° tilt with respect to the mandrel symmetry axis.

It is appreciated that certain features of the invention, which are, for 25 clarity, described in the context of separate embodiments, may also be provided in combination in a single embodiment. Conversely, various features of the invention, which are, for brevity, described in the context of a single embodiment, may also be provided separately or in any suitable 30 subcombination.

Although the invention has been described in conjunction with specific embodiments thereof, it is evident that many alternatives, modifications and variations will be apparent to those skilled in the art.

5 Accordingly, it is intended to embrace all such alternatives, modifications and variations that fall within the spirit and broad scope of the appended claims. All publications, patents and patent applications mentioned in this specification are herein incorporated in their entirety by reference into the specification, to the same extent as if each individual publication, patent or

10 patent application was specifically and individually indicated to be incorporated herein by reference. In addition, citation or identification of any reference in this application shall not be construed as an admission that such reference is available as prior art to the present invention.

## WHAT IS CLAIMED IS:

1. An apparatus for manufacturing polymer fiber shell from liquefied polymer, the apparatus comprising:

- (a) a precipitation electrode being for generating the polymer fiber shell thereupon;
- (b) a dispenser, being at a first potential relative to said precipitation electrode so as to generate an electric field between said precipitation electrode and said dispenser, said dispenser being for:
  - (i) charging the liquefied polymer thereby providing a charged liquefied polymer; and
  - (ii) dispensing said charged liquefied polymer in a direction of said precipitation electrode; and
- (c) a subsidiary electrode being at a second potential relative to said precipitation electrode, said subsidiary electrode being for modifying said electric field between said precipitation electrode and said dispenser.

2. The apparatus of claim 1, wherein said subsidiary electrode serves for reducing non-uniformities in said electric field between said precipitation electrode and said dispenser.

3. The apparatus of claim 1, wherein said subsidiary electrode serves for controlling fiber orientation of said polymer fiber shell generated upon said precipitation electrode.

4. The apparatus according to claim 1, wherein said dispenser comprises a mechanism for forming a jet of said charged liquefied polymer.

5. The apparatus according to claim 1, further comprising a bath for holding the liquefied polymer.

6. The apparatus according to claim 4, wherein said mechanism for forming a jet of said charged liquefied polymer includes a dispensing electrode.

7. The apparatus according to claim 1, wherein said dispenser is operative to move along a longitudinal axis of said precipitation electrode.

8. The apparatus according to claim 1, wherein said precipitation electrode includes at least one rotating mandrel.

9. The apparatus according to claim 8, wherein said rotating mandrel is a cylindrical mandrel.

10. The apparatus according to claim 9, wherein said cylindrical mandrel is of a diameter selected from a range of 0.1 to 20 millimeters.

11. The apparatus according to claim 8, wherein said rotating mandrel is an intricate-profile mandrel.

12. The apparatus according to claim 11, wherein said intricate-profile mandrel includes sharp structural elements.

13. The apparatus according to claim 1, wherein said precipitation electrode includes at least one structural element selected from the group consisting of a protrusion, an orifice, a groove, and a grind.

14. The apparatus according to claim 1, wherein said subsidiary electrode is of a shape selected from the group consisting of a plane, a cylinder, a torus and a wire.

15. The apparatus according to claim 1, wherein said subsidiary electrode is operative to move along a longitudinal axis of said precipitation electrode.

16. The apparatus according to claim 1, wherein said subsidiary electrode is tilted at angle with respect to a longitudinal axis of said precipitation electrode, said angle is ranging between 45 and 90 degrees.

17. The apparatus according to claim 1, wherein said subsidiary electrode is positioned at a distance of 5 - 70 millimeters from said precipitation electrode.

18. The apparatus according to claim 1, wherein said subsidiary electrode is positioned at a distance  $\delta$  from said precipitation electrode,  $\delta$  being equal to  $12\beta R(1-V_2/V_1)$ , where  $\beta$  is a constant ranging between about 0.7 and about 0.9,  $R$  is a curvature-radius of the polymer fiber shell formed on said precipitation electrode,  $V_1$  is said first potential and  $V_2$  is said second potential.

19. A method for forming a liquefied polymer into a non-woven polymer fiber shell, the method comprising:

- (a) charging the liquefied polymer thereby producing a charged liquefied polymer;
- (b) subjecting said charged liquefied polymer to a first electric field;
- (c) dispensing said charged liquefied polymer within said first electric field in a direction of a precipitation electrode, said

precipitation electrode being designed and configured for generating the polymer fiber shell thereupon;

- (d) providing a second electric field being for modifying said first electric field; and
- (e) using said precipitation electrode to collect said charged liquefied polymer thereupon, thereby forming the non-woven polymer fiber shells.

20. The method according to claim 19, wherein said first electric field is defined between said precipitation electrode and a dispensing electrode being at a first potential relative to said precipitation electrode.

21. The method according to claim 20, wherein step (c) is effected by dispensing said charged liquefied polymer from said dispensing electrode.

22. The method according to claim 19, further comprising moving said dispensing electrode along a longitudinal axis of said precipitation electrode during step (c).

23. The method according to claim 19, wherein said precipitation electrode includes at least one rotating mandrel.

24. The method according to claim 23, wherein said rotating mandrel is a cylindrical mandrel.

25. The method according to claim 24, wherein said cylindrical mandrel is of a diameter selected from a range of 0.1 to 20 millimeters.

26. The method according to claim 23, wherein said rotating mandrel is an intricate-profile mandrel.

27. The method according to claim 26, wherein said intricate-profile mandrel includes sharp structural elements.

28. The method according to claim 25, wherein said precipitation electrode includes at least one structural element selected from the group consisting of a protrusion, an orifice, a groove, and a grind.

29. The method according to claim 20, wherein said second electric field is defined by a subsidiary electrode being at a second potential relative to said precipitation electrode.

30. The method according to claim 29, wherein said subsidiary electrode serves for reducing non-uniformities in said first electric field.

31. The method according to claim 19, wherein said subsidiary electrode serves for controlling fiber orientation of said polymer fiber shell generated upon said precipitation electrode.

32. The method according to claim 29, wherein said subsidiary electrode is of a shape selected from the group consisting of a plane, a cylinder, a torus and a wire.

33. The method according to claim 29, further comprising moving said subsidiary electrode along said precipitation electrode during step (e).

34. The method according to claim 29, further comprising tilting said subsidiary electrode at angle with respect to a longitudinal axis of said precipitation electrode, said angle ranging between 45 and 90 degrees.

35. The method according to claim 29, wherein said subsidiary electrode is positioned at a distance of 5 - 50 millimeters from said precipitation electrode.

36. The method according to claim 29, wherein said subsidiary electrode is positioned at a distance  $\delta$  from said precipitation electrode,  $\delta$  being equal to  $12\beta R(1-V_2/V_1)$ , where  $\beta$  is a constant ranging between about 0.7 and about 0.9,  $R$  is a curvature-radius of the polymer fiber shell formed on said precipitation electrode,  $V_1$  is said first potential and  $V_2$  is said second potential.

37. An apparatus for manufacturing a polymer fiber shell from liquefied polymer, the apparatus comprising:

- (a) a dispenser, for:
  - (i) charging the liquefied polymer thereby providing a charged liquefied polymer; and
  - (ii) dispensing said charged liquefied polymer; and
- (b) a precipitation electrode being at a potential relative to said dispenser thereby generating an electric field between said precipitation electrode and said dispenser, said precipitation electrode being for collecting said charged liquefied polymer drawn by said electric field, to thereby form the polymer fiber shell thereupon, wherein said precipitation electrode is designed so as to reduce non-uniformities in said electric field.

38. The apparatus according to claim 37, wherein said dispenser comprises a mechanism for forming a jet of said charged liquefied polymer.

39. The apparatus according to claim 37, further comprising a bath for holding the liquefied polymer.

40. The apparatus according to claim 38, wherein said mechanism for forming a jet of said charged liquefied polymer includes a dispensing electrode.

41. The apparatus according to claim 37, wherein said precipitation electrode is formed from a combination of electroconductive and non-electroconductive materials.

42. The apparatus according to claim 41, wherein a surface of said precipitation electrode is formed from a predetermined pattern of said electroconductive and non-electroconductive materials.

43. The apparatus according to claim 37, wherein said precipitation electrode is formed from at least two layers.

44. The apparatus according to claim 43, wherein said at least two layers include an electroconductive layer and a partial electroconductive layer.

45. The apparatus according to claim 44, wherein said partial electroconductive layer is formed from a combination of an electroconductive material and at least one dielectric material.

46. The apparatus according to claim 45, wherein said dielectric material is selected from a group consisting of polyamide, polytetrafluoroethylene and polyacrylonitrile.

47. The apparatus according to claim 45, wherein said dielectric material is Titanium Nitride.

48. The apparatus according to claim 44, wherein said partially electroconductive layer, is of a thickness selected from a range of 0.1 to 90 microns.

49. The apparatus according to claim 37, wherein said precipitation electrode is of a diameter selected from a range of 0.1 to 20 millimeters.

50. The apparatus according to claim 37, wherein said precipitation electrode includes at least one rotating mandrel.

51. The apparatus according to claim 50, wherein said rotating mandrel is a cylindrical mandrel.

52. A tubular structure manufactured by the apparatus of claim 1.

53. A tubular structure manufactured by the method of claim 29.

54. A tubular structure manufactured by the apparatus of claim 37.

55. The apparatus of claim 1, wherein said subsidiary electrode serves to minimize a volume charge generated between said dispenser and said precipitation electrode.

56. The method according to claim 29, wherein said subsidiary electrode serves to minimize a volume charge generated between said precipitation electrode and said dispensing electrode.

57. The apparatus according to claim 1, wherein said dispenser and said subsidiary electrode are operative to move synchronically along a longitudinal axis of said precipitation electrode.

58. The method according to claim 29, further comprising synchronically moving both said dispensing electrode and said subsidiary electrode along said precipitation electrode.

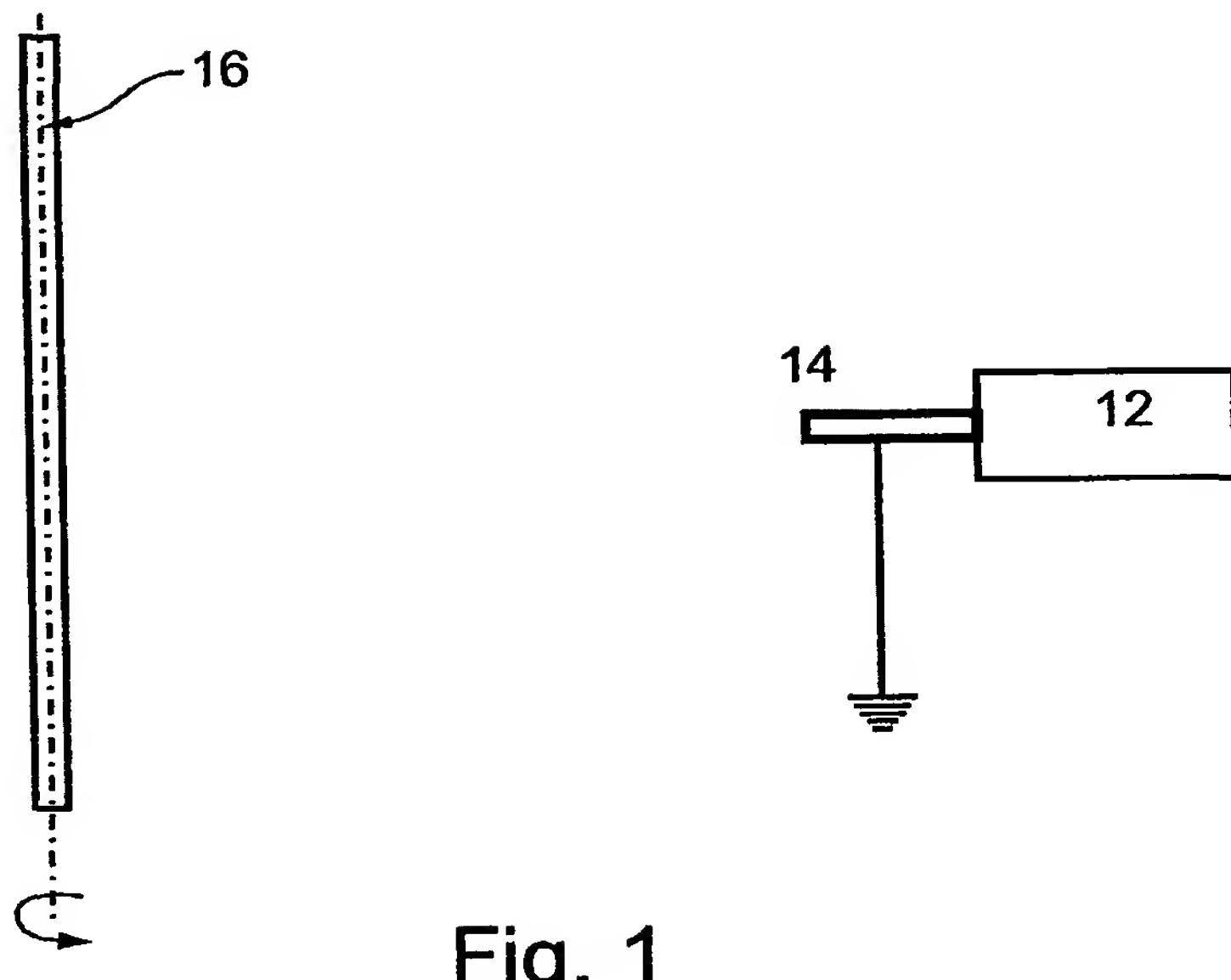


Fig. 1

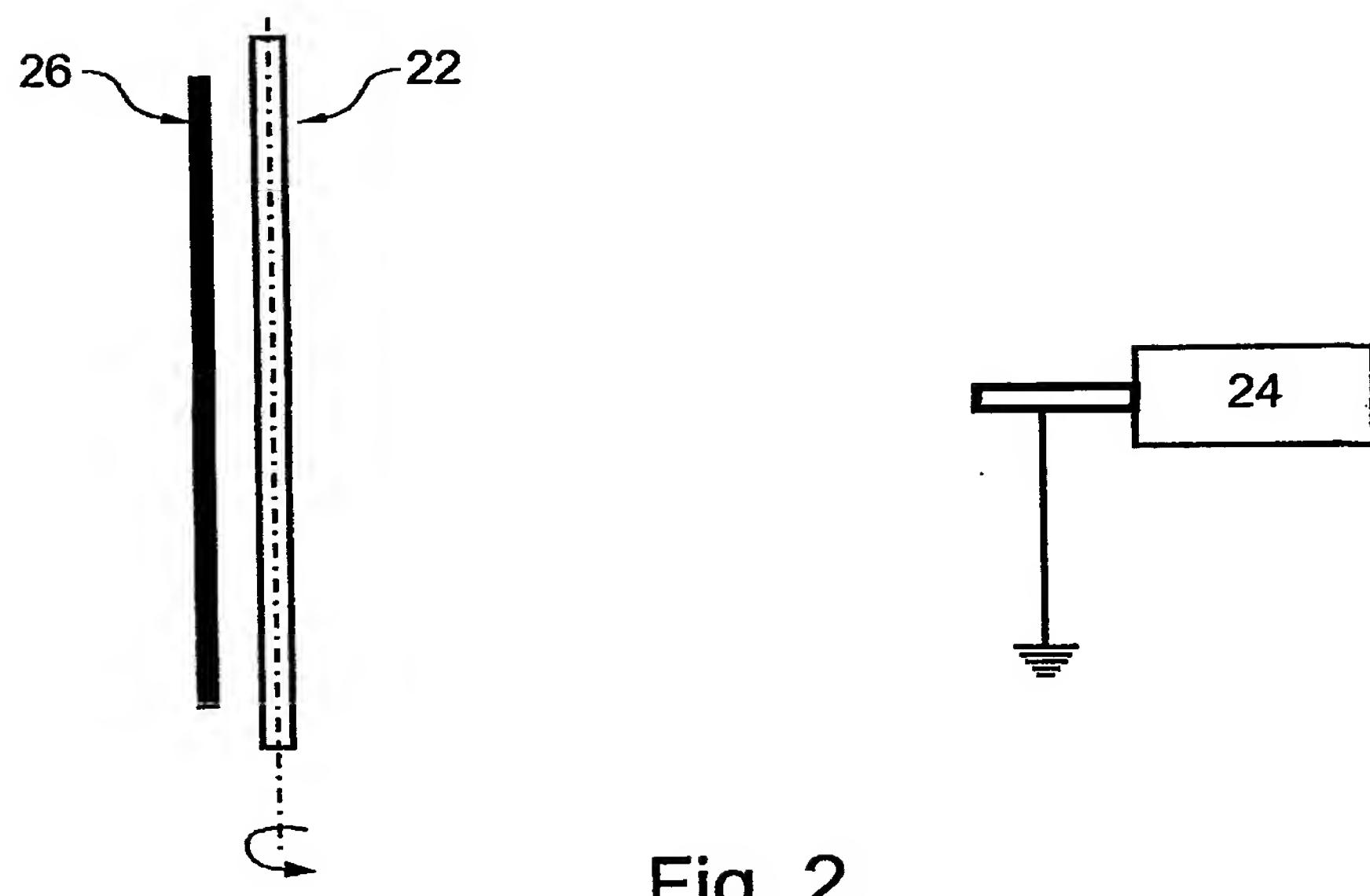


Fig. 2

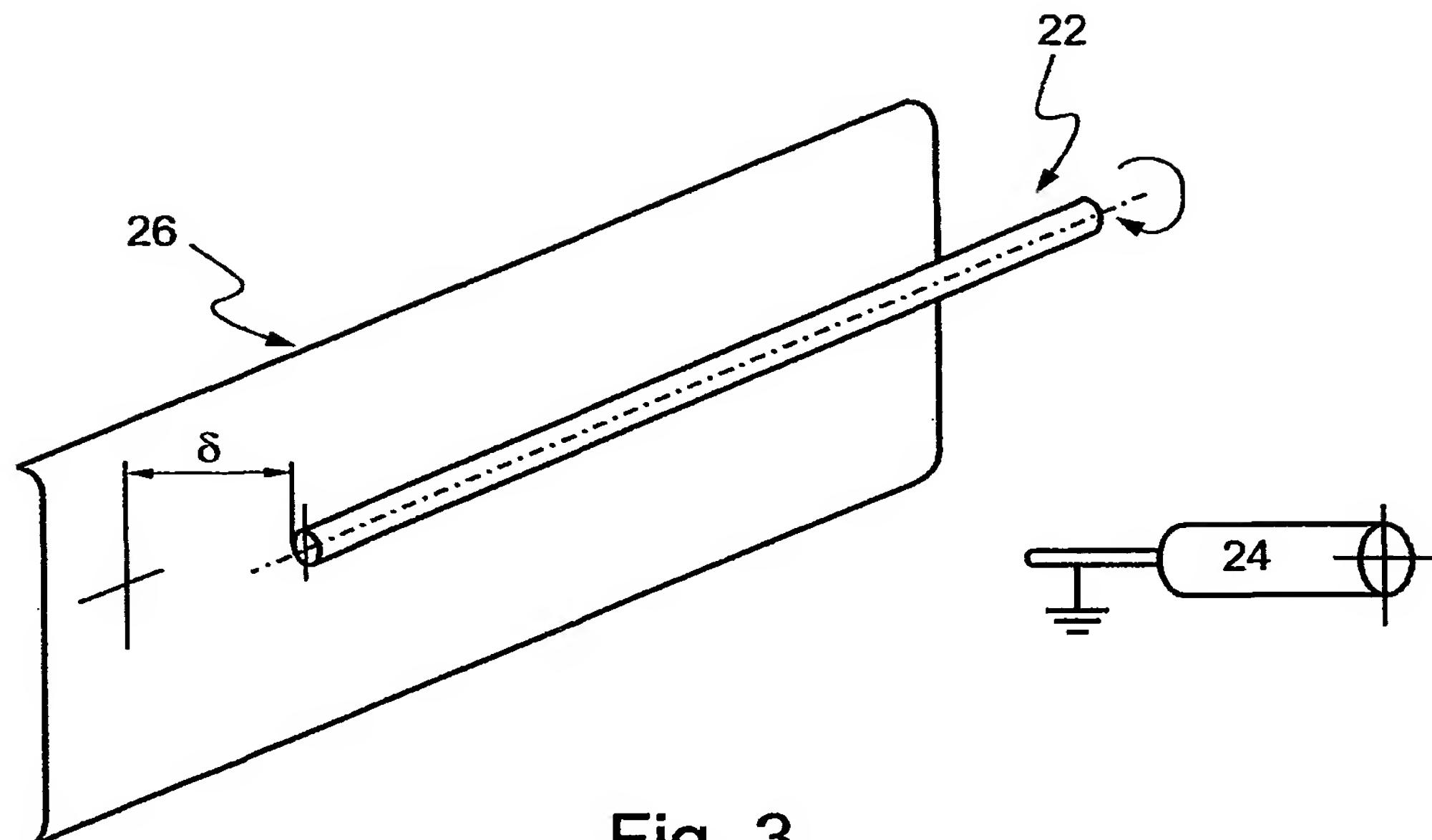


Fig. 3

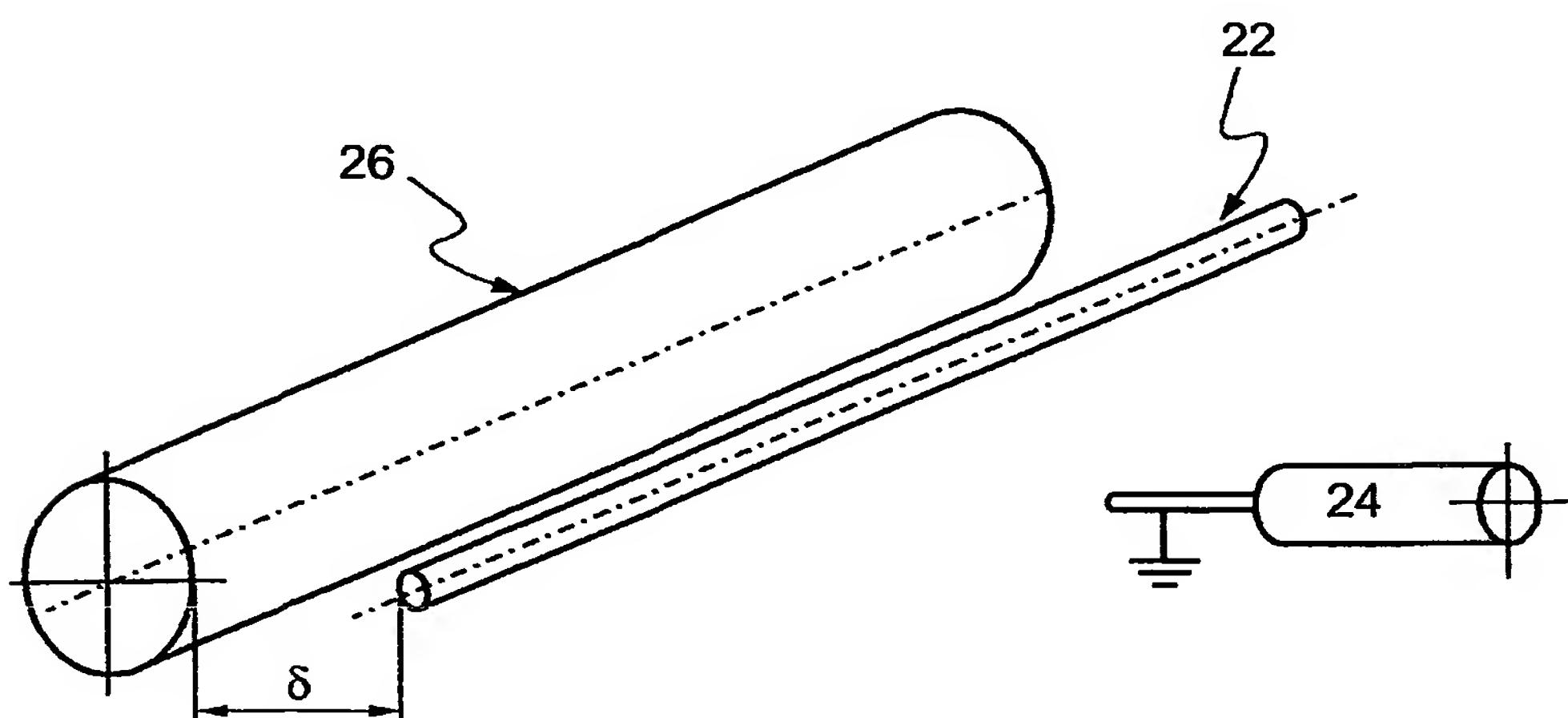


Fig. 4

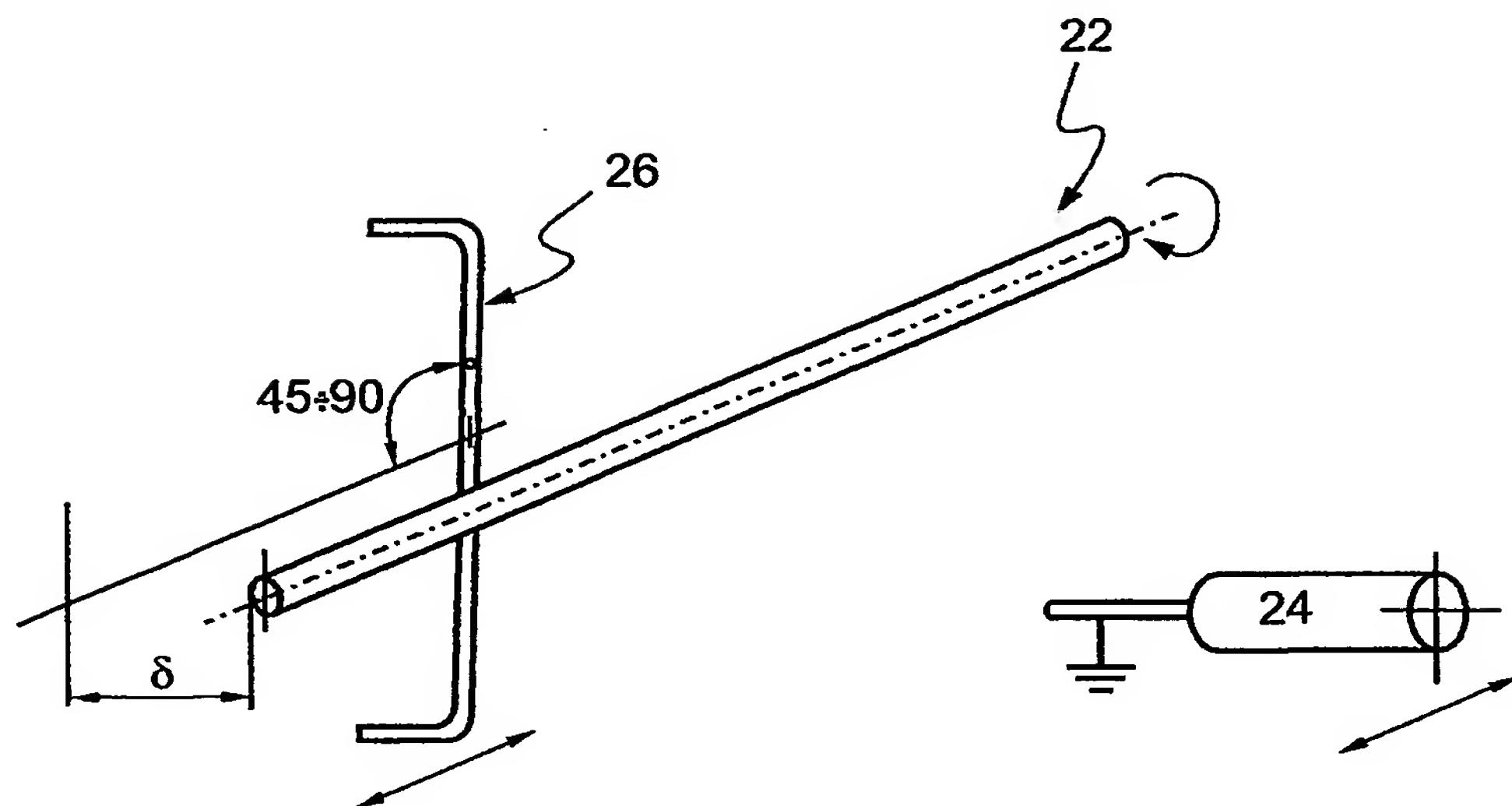


Fig. 5

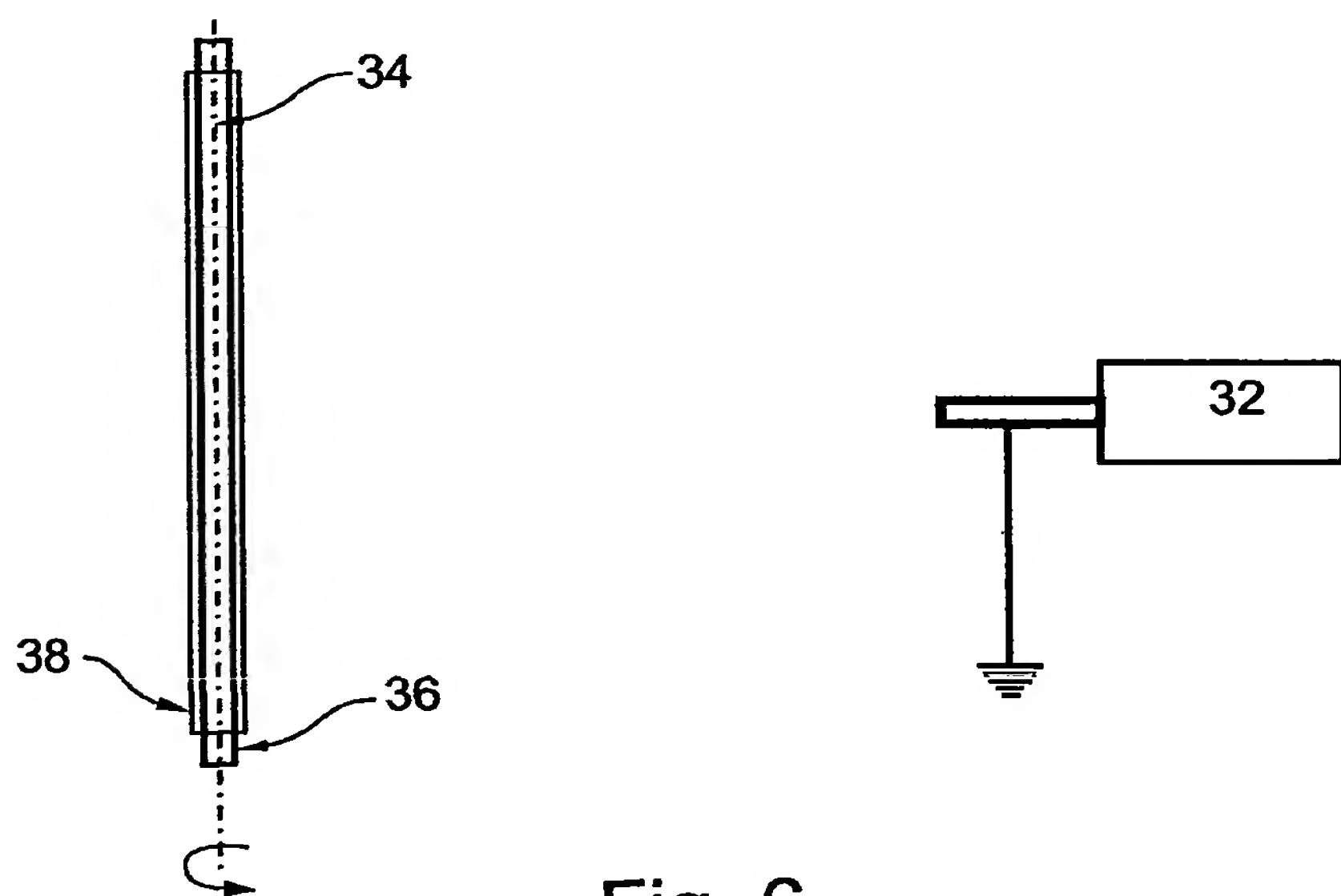


Fig. 6

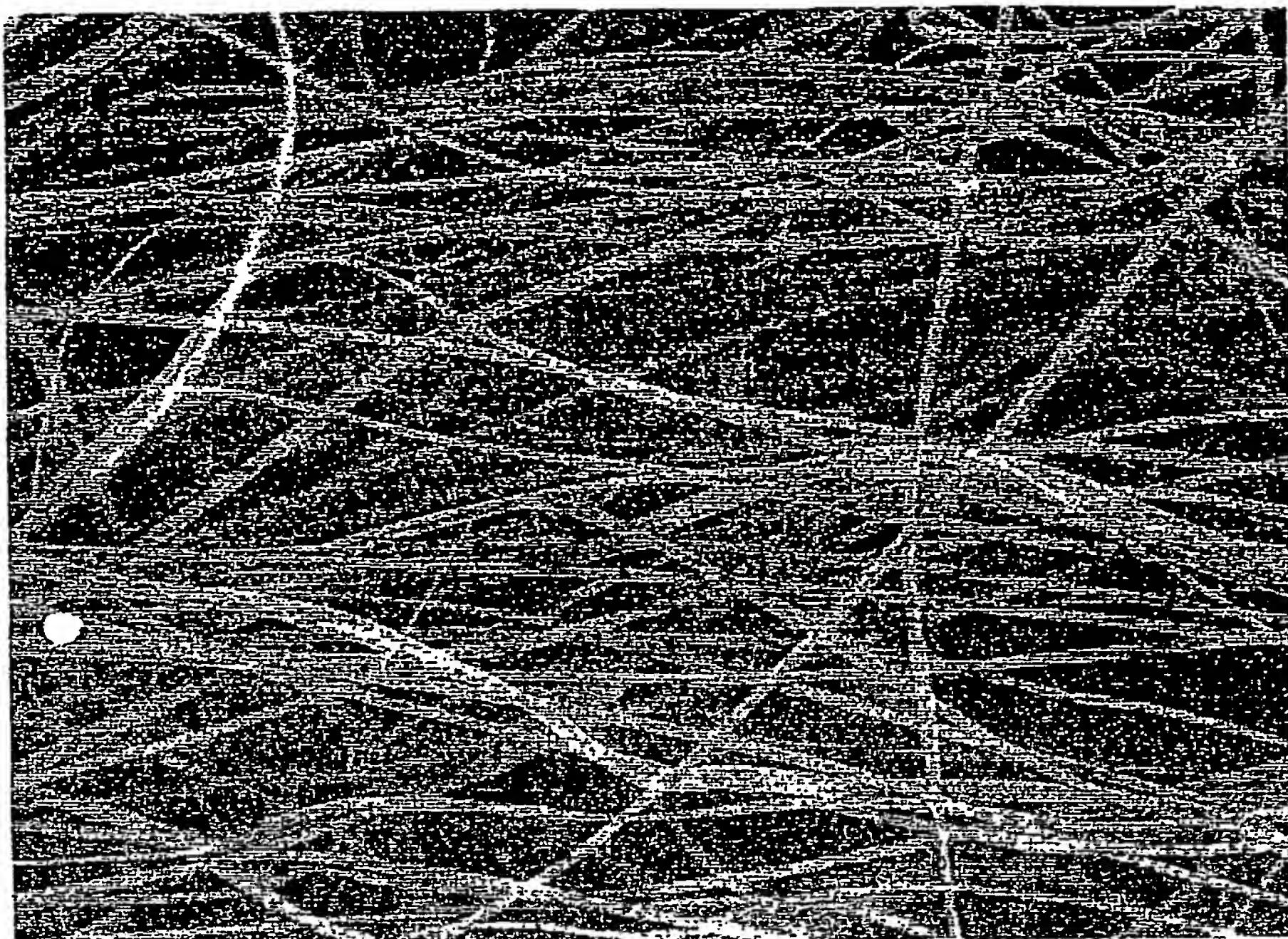


Fig. 7

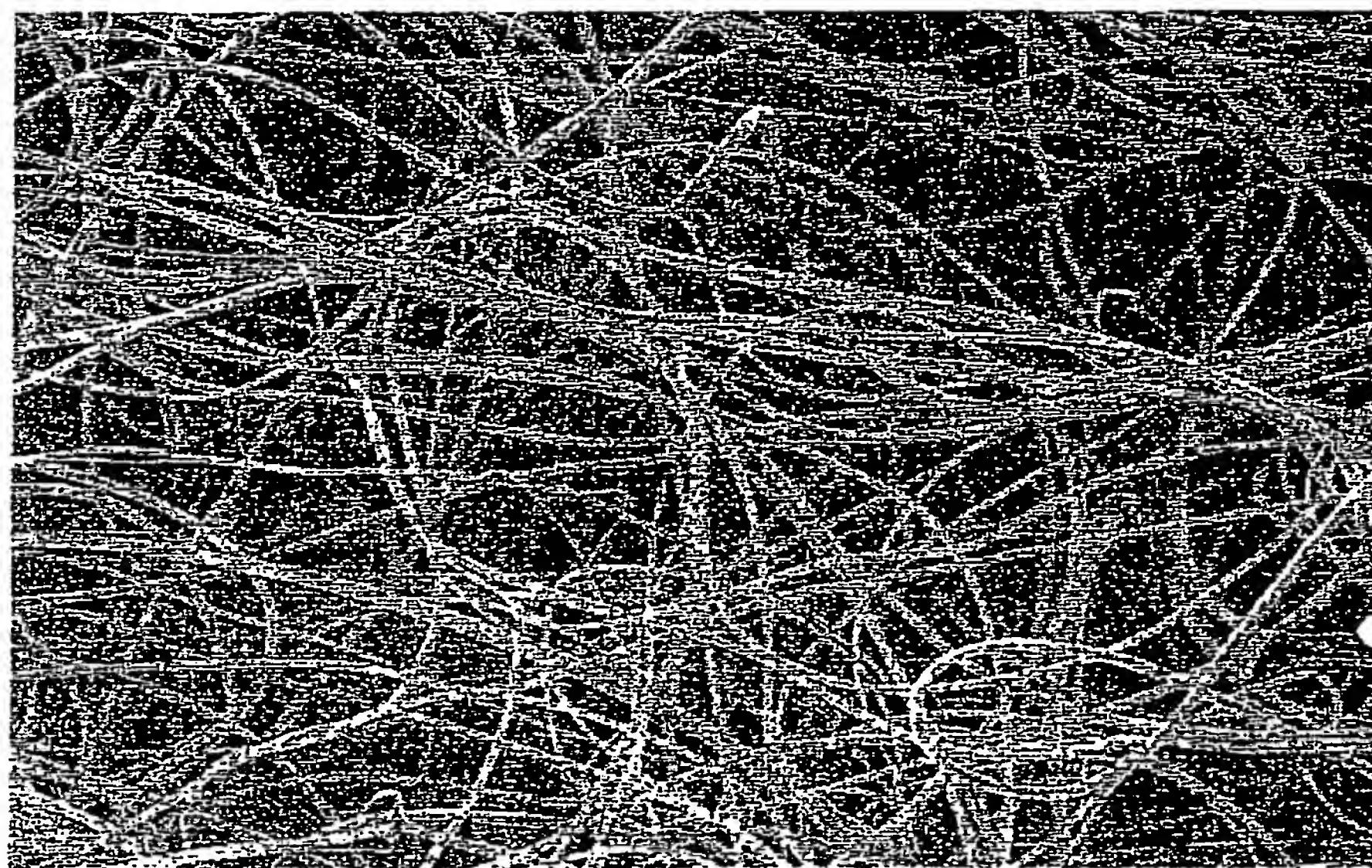


Fig. 8

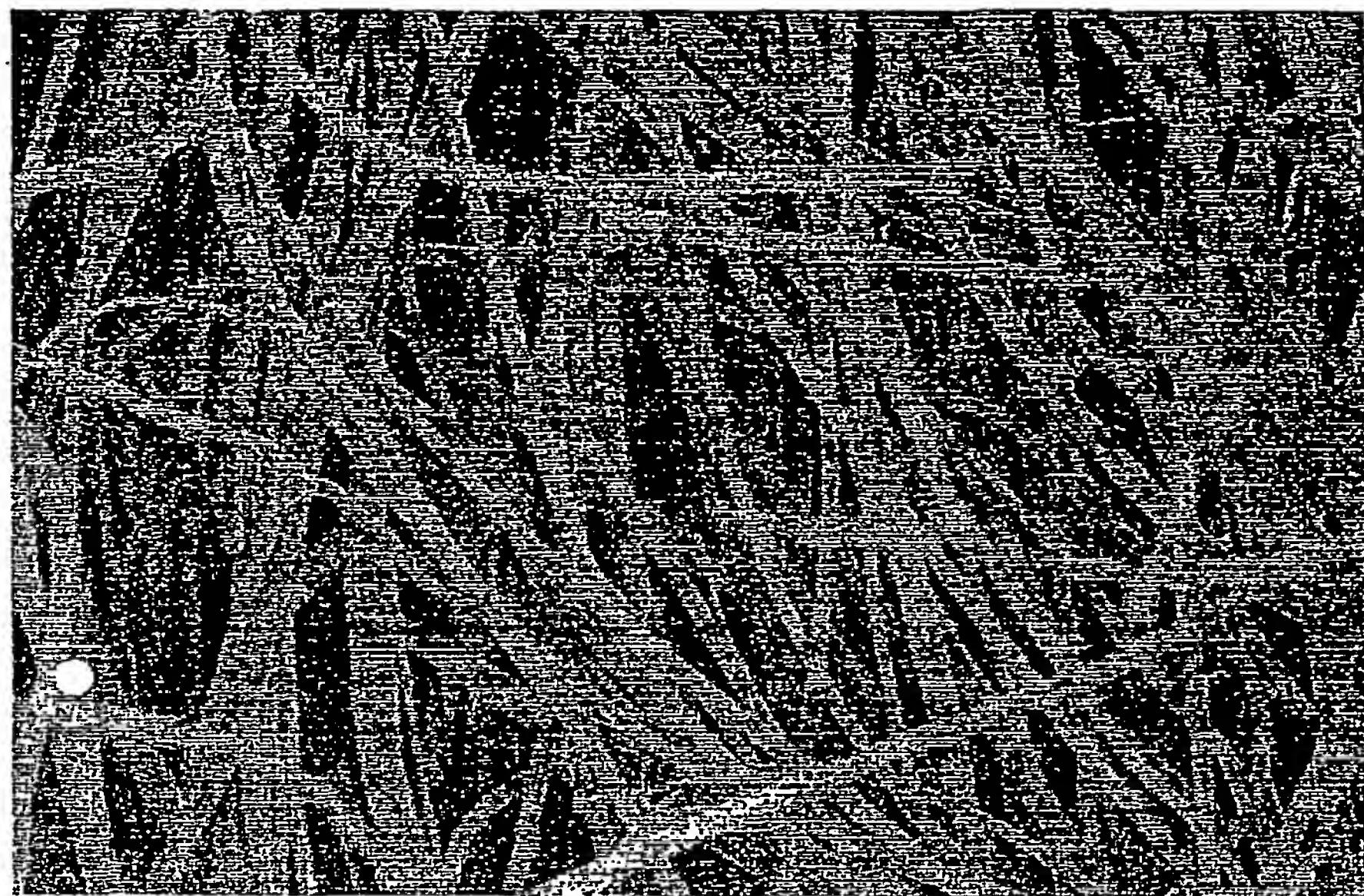


Fig. 9

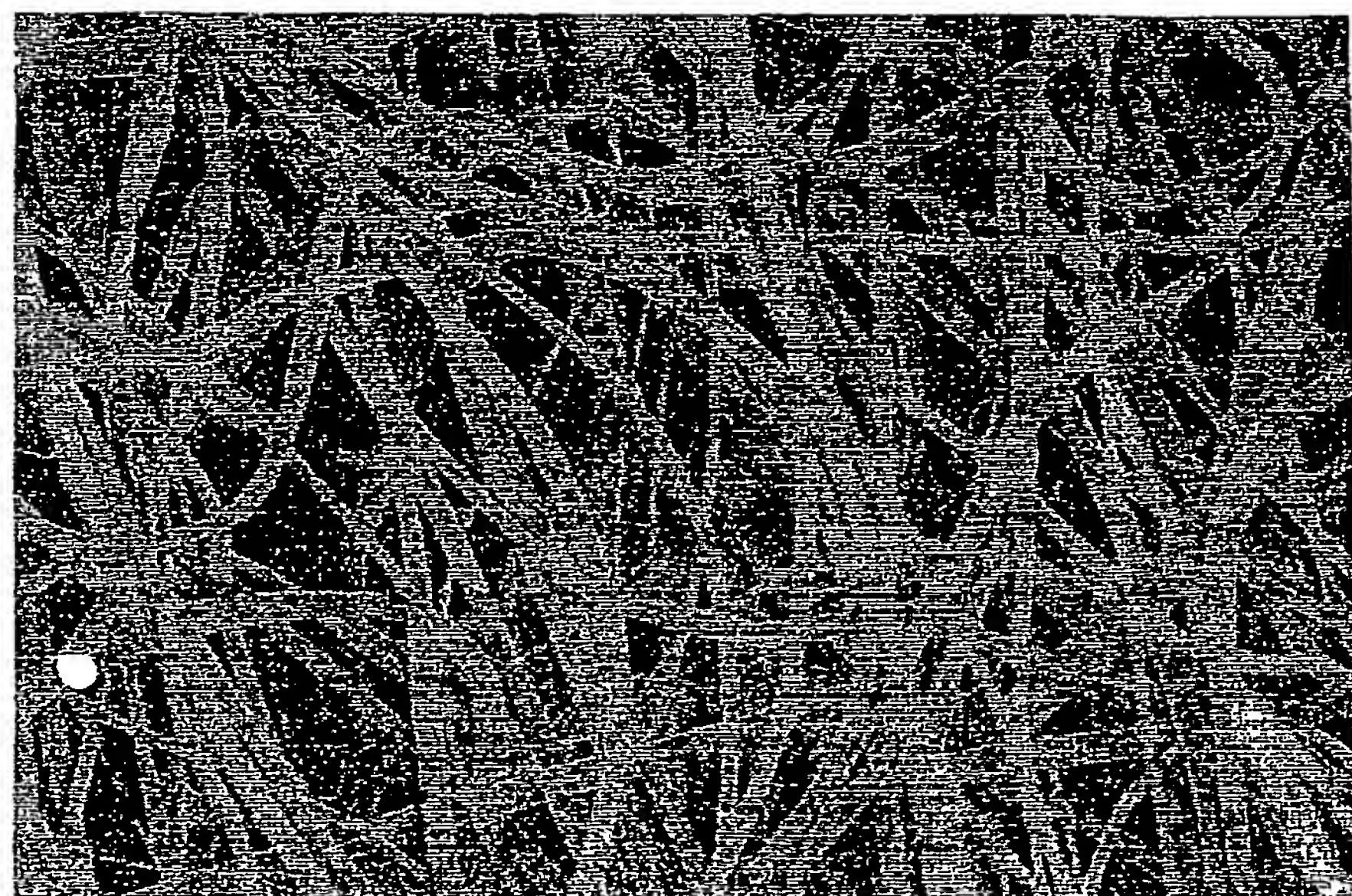


Fig. 10

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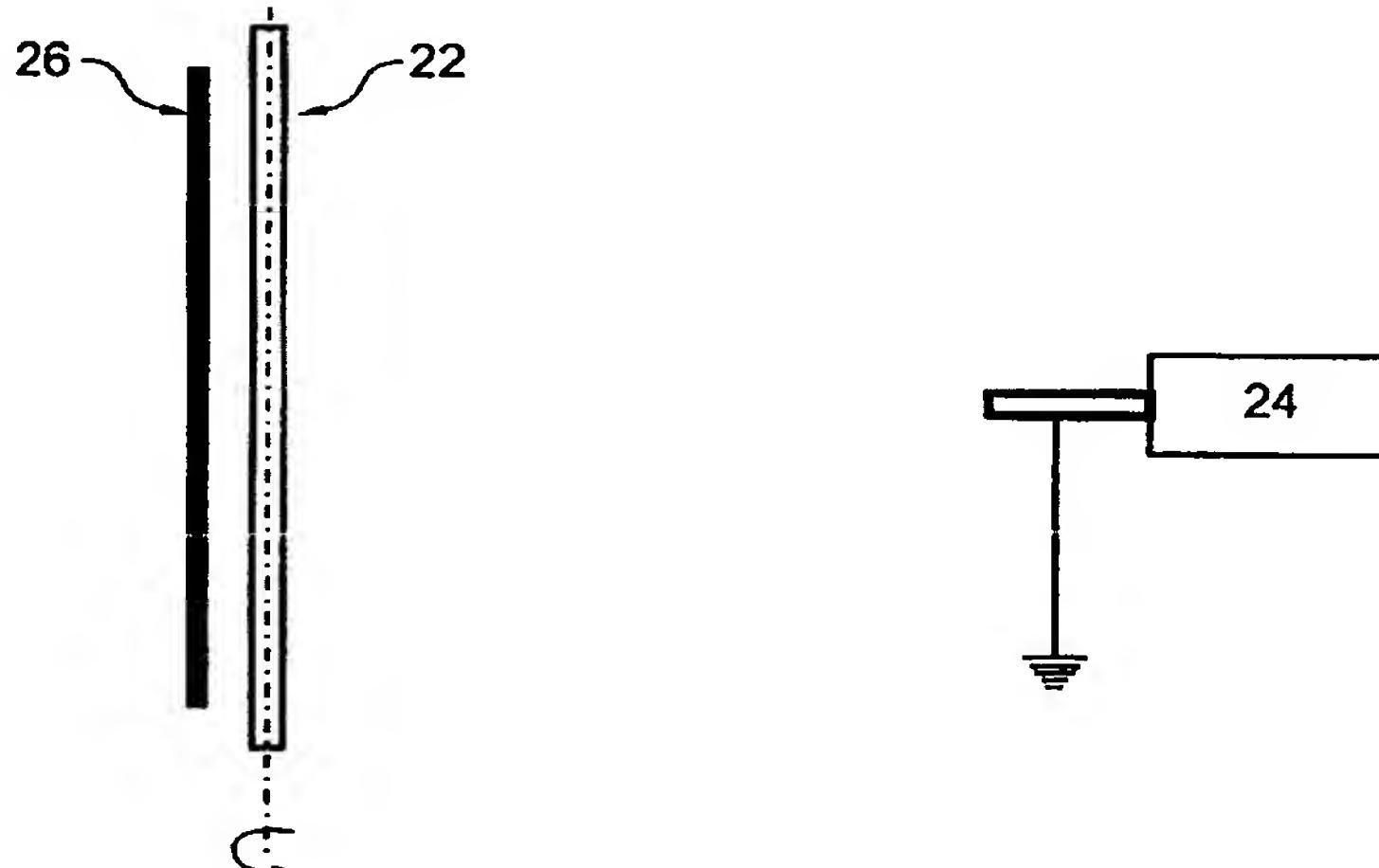
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(54) Title: METHOD AND APPARATUS FOR MANUFACTURING POLYMER FIBER SHELLS VIA ELECTROSPINNING



**WO 02/049678 A3**

(57) Abstract: An apparatus for manufacturing a polymer fiber shell from liquefied polymer is provided. The apparatus includes: (a) a precipitation electrode being for generating the polymer fiber shell thereupon; (b) a dispenser, being at a first potential relative to the precipitation electrode so as to generate an electric field between the precipitation electrode and the dispenser, the dispenser being for: (i) charging the liquefied polymer thereby providing a charged liquefied polymer; and (ii) dispensing the charged liquefied polymer in a direction of the precipitation electrode; and (c) a subsidiary electrode being at a second potential relative to the precipitation electrode, the subsidiary electrode being for modifying the electric field between the precipitation electrode and the dispenser.

WO 02/049678 A3



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3 January 2003

*For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(15) Information about Correction:

Previous Correction:

see PCT Gazette No. 40/2002 of 3 October 2002, Section II

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/IL01/01168

**A. CLASSIFICATION OF SUBJECT MATTER**

IPC(7) : B29B 013/08

US CL : 264/484; 425/174.8E

According to International Patent Classification (IPC) or to both national classification and IPC

**B. FIELDS SEARCHED**

Minimum documentation searched (classification system followed by classification symbols)

U.S. : 264/484,10,441; 425/174.8E,174.8R;427/458,472

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

**C. DOCUMENTS CONSIDERED TO BE RELEVANT**

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 4,689,186 A (Bornat) 25 August 1987 (25.08.1987), Figs 1-6, col 3, lines 37-47 and col 6, lines 3-35.	1-5, 7-20, 22-36, 52-53, 55-58
X	US 3,860,369 A (Brethauer et al) 14 January 1975 (14.01.1975), Figure 1.	1-6, 8, 11-13, 16, 19-21, 23, 26-31, 34, 55-56

 Further documents are listed in the continuation of Box C.

See patent family annex.

\* Special categories of cited documents:

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier application or patent published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art

"&amp;" document member of the same parent family

Date of the actual completion of the international search

Date of mailing of the international search report

14 July 2002 (14.07.2002)

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**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/IL01/01168

**Box I Observations where certain claims were found unsearchable (Continuation of Item 1 of first sheet)**

This international report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1.  Claim Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
  
2.  Claim Nos.:  
because they relate to parts of the international application that do not comply with the prescribed requirements to such an extent that no meaningful international search can be carried out, specifically:
  
3.  Claim Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

**Box II Observations where unity of invention is lacking (Continuation of Item 2 of first sheet)**

This International Searching Authority found multiple inventions in this international application, as follows:  
Please See Continuation Sheet

1.  As all required additional search fees were timely paid by the applicant, this international search report covers all searchable claims.
2.  As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3.  As only some of the required additional search fees were timely paid by the applicant, this international search report covers only those claims for which fees were paid, specifically claims Nos.:
  
4.  No required additional search fees were timely paid by the applicant. Consequently, this international search report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.: 1-36, 52-53 and 55-58

Remark on Protest

The additional search fees were accompanied by the applicant's protest.

No protest accompanied the payment of additional search fees.

**INTERNATIONAL SEARCH REPORT**

International application No.

PCT/IL01/01168

**BOX II. OBSERVATIONS WHERE UNITY OF INVENTION IS LACKING**

Group I, claim(s) 1-36, 52-53 and 55-58, drawn to a method and apparatus for making a fiber shell and using a subsidiary electrode.

Group II, claim(s) 37-51 and 54, drawn to an apparatus for making a fiber shell using a precipitation electrode designed to reduce non-uniformities in the electric field.

The inventions listed as Groups I and II do not relate to a single general inventive concept under PCT Rule 13.1 because, under PCT Rule 13.2, they lack the same or corresponding special technical features for the following reasons: All of the groups are directed to method and apparatus useful in the general field of producing a fiber shell, but each group has different special technical features. Group I has a special technical feature directed to a subsidiary electrode to modify a first electric field between a precipitation electrode and a dispenser not required for Group II. Group II has a special technical feature directed to precipitation electrode that is designed to reduce non-uniformities in the electric field.